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IN THE KJELDAHL DETERMINATION. A NEW  
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In a study to modify the Kjeldahl method for nitrogen so that it would be suitable for all types of nitrogenous organic compounds, inconsistent "blank" values were obtained even when the same reagents were used. Since the nitrogen "blank" values should be constant for any set of reagents, this inconsistency could be accounted for only by assuming that droplets of the alkaline reaction mixture were entrained in the vapors and carried through the Kjeldahl connecting bulb. The same difficulty was experienced with several commonly used connecting bulbs which have either been described in the literature (1, 3, 4,) or listed as catalogue items. This "distillation" of nonvolatile alkali had been recognized previously by Davisson (1) and by Lovecy (4). The variation of the "blank" depends upon the efficiency of the bulb in removing droplets of entrained alkali from the vapor stream and upon the concentration of the droplets in the vapor caused by the reagent or by the rate of distillation. The blank, therefore, becomes a possibly serious source of error in the Kjeldahl method for the determination of nitrogen. Obviously, with a varying blank, the selection of the correct blank becomes impossible. It does not necessarily follow that reproducible blank values are correct, since the conditions of the distillation of the samples and blank may be different. To eliminate this nonvolatile alkali error and still permit complete recovery of ammonia, a new connecting bulb has been designed, and has been used satisfactorily during the past year as part of a 24-unit Kjeldahl apparatus in which a large number of nitrogen determinations were made.

*Description of bulb.*—The new connecting bulb (Fig. 1) is unique in that it has two wire screens, which serve as condensers to form water films at the beginning of the distillation, as plates to support the condensed water, and as diffusors of the distilled vapors.

The application of the countercurrent extraction principle to Kjeldahl connecting bulbs is not new. Davisson (1) made use of this principle, but his bulb failed in that it did not start to scrub the vapors until sufficient distillate had collected in the bulb to cover the holes in the small inner bulb. During this time any droplets that occurred in the vapor were free to be carried through the bulb by the vapor stream. Lovecy (4) also made use of this principle, but unless the distillation rate was kept slow the scrubbing action was not effective and the condensate was carried over into the receiver.

\* Presented at the Annual Meeting of the Association of Official Agricultural Chemists, held at Washington, D. C., October 20-22, 1947.

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The experimental connecting bulb scrubs all the vapors passing through it, since a water film forms on the wire screen plates the instant water vapor reaches them, and these films are maintained throughout the distillation. In passing through the layer of water condensate built up on the upper screen plate, the vapors carry water into the bulb vapor trap. The amount of condensate carried into the bulb seldom exceeds 35 ml., even with long distillation times.

The condensate in the bulb is maintained above pH 7 by the nonvolatile alkali scrubbed from the vapor, and it is kept at or near the boiling point by the passing steam. Under these conditions, no ammonia should be retained in the condensate in the connecting bulb. That no ammonia was retained was confirmed by collecting the bulb condensate at the end of a nitrogen determination and testing it with Nessler's reagent.

A comparison was made of four of the commonly used Kjeldahl connecting bulbs with the experimental bulb. The Lovecy bulb was not considered in these tests because of its fragile structure and because of the care that must be exercised in controlling the necessarily slow distillation rate.

The distillation mixture consisted of 100 ml of 50 per cent sodium hydroxide, which had been boiled to remove any ammonia, 250 ml of water and 10 grams of mossy zinc. Two hundred milliliters of distillate were collected in receivers containing 50 ml of 0.0100 *N* hydrochloric acid at the rate of 100 ml in 30 minutes for the slow distillation and 200 ml in 30 minutes for the rapid distillation. This test mixture, which is similar to that used by Davisson, produces a heavy spray rich in nonvolatile alkali. The results are given in Table 1.

The zinc was responsible for the large amounts of sodium hydroxide in the vapor, since when no zinc was used in the distillation mixture, the amount of sodium hydroxide carried over was small and nearly independent of the type of bulb used. The form of the zinc was also an important factor, since mossy zinc caused almost twice as much sodium hydroxide to be carried over as did an equal weight of 20-mesh zinc.

In these tests, those bulbs which did not provide for scrubbing the distilled vapors (the Hopkins, Iowa State and the Kjeldahl) passed the largest amount of sodium hydroxide. The poorest duplicate check results were obtained with the bulbs which passed the most sodium hydroxide. Of the nonscrubbing-type connecting bulbs the Hopkins bulb allowed the greatest amount of sodium hydroxide to pass and the Kjeldahl bulb the least. Much less nonvolatile alkali passed through the two scrubbing-type bulbs. The experimental bulb was more than three times as effective as the Davisson and more than thirteen times as effective as the best nonscrubbing type. These data indicate that bulbs having only baffles are ineffective, and when used, the conditions of the distillation must be controlled to give a minimum amount of droplets in the vapor stream. Only

those bulbs which scrub the vapors will perform satisfactorily independent of the distillation conditions.

Using the Davisson scrubber, the best of the common connecting bulbs, as shown by the preceding experiment, the blank values obtained under ordinary Kjeldahl conditions ranged from a low of 0.2 ml to a high of 0.6 ml of 0.1 *N* hydrochloric acid. The experimental connecting bulb under

TABLE 1.—Comparison of various types of Kjeldahl connecting bulbs for removal of entrained nonvolatile alkali

BULB	DISTILLATION OF 200 ML. PER 30 MIN.			DISTILLATION OF 100 ML PER 30 MIN.	
	WITH MOSBY ZINC	WITH 20-MESH ZINC	WITHOUT ZINC	WITH MOSBY ZINC	
<i>Scrubber Type</i>					
Experimental bulb	1.82* 1.89 Ave. 1.9	1.30 1.12 Ave. 1.2	1.33 1.06 Ave. 1.2	1.40* 1.68 Ave. 1.5	
Davisson bulb	5.69 6.45 Ave. 6.1	3.00* 2.60 Ave. 2.8	1.57* 1.72 Ave. 1.7	2.79 3.67 Ave. 3.2	
<i>Nonscrubber Type</i>					
Kjeldahl bulb	23.02 26.92 Ave. 24.9	2.16 1.36 Ave. 1.8		19.4 24.0 Ave. 21.7	
Iowa State bulb	56.96 69.93 Ave. 63.5	91.14 36.89 Ave. 64	1.67 1.83 Ave. 1.8	77.0 61.0 Ave. 69.0	
Hopkins bulb	152.0 161.0 Ave. 156	164.0 187.0 Ave. 176		64.0 210.0 Ave. 137	

\* Amount of nonvolatile alkali carried to the receiver expressed as milliliters of 0.01 *N* HCl.

the same conditions gave a blank value of 0.0 to 0.04 ml of 0.1 *N* hydrochloric acid.

An attempt was made to evaluate the two parts of the new bulb, the screen plates and the bulb trap, but it was found that the values obtained by independent measurements of each part were of little significance and that the bulb could be considered only as a whole. The bulb was especially useful as an antifoam trap. In this respect it was far superior to the other bulbs tested.

The rate at which ammonia was distilled into the receiver was determined by preparing several Kjeldahl flasks, all containing the same amounts of reagents and sample. After digestion, alkali was added, and

the ammonia distilled into boric acid. The rate of distillation, 200 ml per 30 minutes, was the same for all flasks. The receiving flasks were then withdrawn at different time intervals, beginning at  $7\frac{1}{2}$  minutes from the start of boiling. The results are given in Table 2. At the rate of 200 ml per 30 minutes, essentially all the nitrogen as ammonia was distilled during the first 22.5 minutes, and a prolonged distillation did not yield appreciably higher values.

TABLE 2.—Rate of distillation of ammonia from Kjeldahl digestion mixtures

DISTILLATION TIME (MIN.)	VOLUME DISTILLED ML. (APPROX.)	NITROGEN FOUND, PER CENT	PER CENT OF TOTAL (THEORY) NITROGEN DISTILLED
7.5	50	$\left\{ \begin{array}{l} 7.96 \\ 7.93 \\ \text{Ave. } 7.94 \end{array} \right.$	95.9
15.0	100	$\left\{ \begin{array}{l} 8.19 \\ 8.12 \\ \text{Ave. } 8.16 \end{array} \right.$	98.6
22.5	150	$\left\{ \begin{array}{l} 8.25 \\ 8.26 \\ \text{Ave. } 8.26 \end{array} \right.$	99.8
30.0	200	$\left\{ \begin{array}{l} 8.26 \\ 8.31 \\ \text{Ave. } 8.29 \end{array} \right.$	100.1
37.5	250	$\left\{ \begin{array}{l} 8.25 \\ 8.23 \\ \text{Ave. } 8.24 \end{array} \right.$	99.5

Tests were also made to determine whether any ammonia was lost during the initial heating period by being carried through the trapping liquid in the large bubbles of the displaced air. Using distilled water and indicator, we demonstrated that no ammonia was carried by the displaced air, since the indicator did not change color until condensed water vapor had reached the receiver. Loss of ammonia by this cause is therefore improbable.

Although the new bulb made it possible to measure accurately the nitrogen blank of the reagents, it did not account for the slightly low nitrogen values obtained on analysis of pure nitrogenous compounds. This loss could be accounted for only by assuming that all the ammonia was not being caught by the trapping liquid. In an attempt to eliminate this source of error, a Goessman trap (2) was used on the receiver. Results of analyses of S-benzyl thiuronium chloride with the new connecting bulb, with and without the Goessman trap, are given in Table 3. The Goessman

trap caused an increase of 0.5 per cent of the total nitrogen found when boric acid was the trapping liquid and 0.7 per cent when 0.1 *N* hydrochloric acid was used. Results most closely approximating the theoretical were obtained when boric acid was used.

Of the many mixed indicators proposed in the past few years, a mixture of methyl red and methylene blue is often used in Kjeldahl nitrogen titrations. This indicator has been used in many proportions of methyl red to methylene blue, but 4 parts of methyl red to 1 part of methylene blue, with a final concentration of methyl red of 0.1 per cent wt./vol. in 95% alcohol was the most satisfactory with boric acid. Under these conditions

TABLE 3.—*Nitrogen analysis of S-benzyl thiuronium chloride\* by the Kjeldahl method with a new connecting bulb*

LIQUID IN RECEIVER	WITH GOESSMAN TRAP		WITHOUT TRAP	
	NITROGEN, %	RECOVERY, %	NITROGEN, %	RECOVERY, %
Boric acid	13.80		13.82	
	13.78		13.81	
	13.84		13.70	
	13.81		13.78	
	13.81		13.76	
	13.80		13.70	
	Ave. 13.81	99.9	Ave. 13.76	99.6
HCl 0.1 <i>N</i>	13.73		13.63	
	13.72		13.66	
	13.70		13.56	
	13.76		13.60	
	13.75		13.64	
	13.67		13.57	
	Ave. 13.72	99.3	Ave. 13.61	98.5

\* % Nitrogen found by the Dumas method equals 13.82.

ammonium hydroxide is titrated with the mineral acid, usually hydrochloric. The grey, neutral color of this mixed indicator coincides exactly with the stoichiometric end point (*pH* 4.7). A 4% boric acid solution, however, is acid to the above mixed indicator, and a correction must be made for this in the determination. By the use of the proposed connecting bulb, or by observing the necessary precautions with reagents suitable for Kjeldahl nitrogen analysis, the alkali distilled in the blank is not sufficient to neutralize the boric acid. The acidity of the boric acid of the blank may be neutralized by back titration with a standard base, but a standard base tends to nullify most of the advantages of boric acid as the trapping liquid. The standard base can be omitted if the color of the indicator in the partially neutralized boric acid of the blank is taken as the end-point color. It will be found that this slightly acid shade of the indicator

(pH 4.2) is easily matched, and in the analysis of a sample the titration will be carried through indicator color changes from green to grey to light purple (end point shade). The grey shade serves as a warning of the approach to the end point. By taking the sample titration to the same indicator color as that developed in the blank, no blank correction need be used in the calculation, since this procedure automatically corrects for the reagent nitrogen and the boric acid acidity.

#### SUMMARY

Some of the sources of errors which occur during distillation in the Kjeldahl method for determination of nitrogen have been pointed out. Chief among these is the carry-over of nonvolatile alkali from the alkaline distilling mixture to the trapping liquid in the receiver. By the use of a new connecting bulb, the carry-over of non-volatile alkali is greatly reduced, practically eliminating this source of error. A titration technique is proposed with the mixed indicator, methyl red-methylene blue, which eliminates the standard base and simultaneously corrects for any base from the reagents as well as for the acidity of the boric acid.

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